# THE OCCURRENCE AND AVAILABILITY OF THE POTASSIUM

# IN SOME SCOTTISH SOILS.

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# I. HISTORICAL.

## A. OCCURRENCE.

### (1) As a Constituent of Soil Minerals.

The element potassium is present in considerable quantity in most soils, particularly those derived from igneous rock formations, existing chiefly as a constituent of the potash felspars and micas. PLUMMER (35) found the order of solubility in carbonated water of the common potash bearing minerals to be biotite, muscovite, orthoclase and microcline. HART (14) in a recent mineralogical examination of the fine sand fractions of a group of soils from the South-East of Scotland, found these minerals to be present in varying amount. Since the more resistant minerals, biotite, orthoclase and muscovite, were usually comparatively fresh and unweathered, it does not follow that the large reserve of potash in those soils will be accompanied by a high degree of availability.

### (2) As a Constituent of Exchangeable Base Content of Soil.

In 1850 WAY (46) showed that a part of the total base content of a soil is displaced on treating the soil with a solution of a neutral salt, and within the last few years this observation has been confirmed by many workers and it is now recognised that this property is related to the colloidal fraction of the soil and it is assumed that the cations capable of replacement or exchange by other cationic radicles /

radicles are adsorbed by an acidic colloidal complex which may be of alumino-silicate or organic composition. Several methods for the separation and estimation of the exchangeable bases have been devised during the last few years, and the importance of the relative base proportions in determining the physical and chemical characteristics of a soil has been emphasised by several workers.

Potassium comprises only a comparatively small fraction of the total exchangeable base content of a normal soil. SMITH (43) has found for a series of Scottish soils an average content of 0,242 milligram equivalents per 100 gms. air dry soil, which represents 2.15% of the total exchangeable base content.

## B. METHODS OF ESTIMATION OF THE TOTAL AND "AVAILABLE" POTASSIUM.

### (1) Total Potassium.

#### (a) Total Mineral Content.

It is comparatively simple to determine the total quantity of potassium in a soil by any of the methods standardised in mineralogical analysis. In the present investigation the Lawrence-Smith method has been preferred to the hydrofluoric acid method.

(b) /

(b) Potassium soluble in solutions of Hydrochloric Acid.

Treatment of the soil with a solution of a strong mineral acid has been used to determine the amount of potassium which is likely to become available to the plant as distinct from the quantity available at any particular moment. LOUGHBRIDGE (24) found that in a single extraction with hot hydrochloric acid of specific gravity 1.115 the quantities of bases extracted increased with the time of extraction up to a limit of five days. HILGARD (17) and A.J. VON SIGMOND (42) have suggested that the five day treatment is the most suitable for soil examination. HISSINK (18), however, does not agree that a limit of solubility is reached after five days' boiling since small quantities of bases go into solution so long as undecomposed mineral fragments remain. He considers that a shorter treatment with hot strong hydrochloric acid differentiates between the silicate groups obtained by VAN BEMMELEN (4) in his examination of lateritic soils. Van Bemmelen divided the soil silicates into two groups - (1) the unweathered mineral fragments occurring as crystals, and (2) the weathered amorphous silicates which could be sub-divided into silicate A, completely decomposed by boiling hydrochloric acid and which could be regarded as an absorption complex of $SiO_2$ with bases rather than a definite chemical compound, and silicate B which is not affected by treatment with hydrochloric acid. Hissink showed that the power of the soil to adsorb bases was destroyed after two hours boiling with hot concentrated hydrochloric acid, and he /

he maintained that this time of extraction was sufficient to give the best estimation of the composition of the adsorbing complex or silicate A.

Extraction with a 10% solution of HCl has been recommended by LEMMERMANN (20) and both 10% and 25% solutions are used as the official methods by the "Verband Landwirtschaftlicher Versuchs-stationen" in Germany. The standard English method adopted by the Agricultural Education Association makes use of concentrated acid reduced by boiling to a concentration of approximately 20.2% HCl. In all the treatments with concentrated solutions of HCl the values obtained depend on the analytical conditions.

### (2) Exchangeable Potassium.

Various cations may be used to effect replacement of the adsorbed potassium, but for analytical convenience salts of ammonium are frequently used. Hydrion, in dilute solutions of hydrochloric or acetic acids, has also been used. MATTSON (25) has shown that the adsorbed bases are displaced by hydrion during electrodialysis and BRADFIELD (5) has designed a convenient two-compartment cell which makes use of the endosmotic property of an alundum thimble to obtain a continuous separation of the dialysate.

### (3) 'Available' Potassium.

It is customary to apply the term 'available' to that fraction of the total quantity of potassium in the soil from which /

which the plant obtains its supply of this nutrient without postulating whether there is any corresponding chemical distinction. Most of the methods used by Agricultural Chemists for estimating the available potassium are based on the assumption that this fraction must be readily soluble and can be determined by treating the soil with a dilute acid.

(a) Citric Acid and other Weak Acid Methods.

DYER (7) suggested the treatment of the soil with a one per cent solution of citric acid, basing his method on the assumption that the plant roots excreted sap of a corresponding degree of acidity which exerted a solvent action on the soil minerals. His method has continued in use as a result of the fairly good agreement which was found to exist between the results of the citric acid extraction and the results of field manurial experiments. HALL and PLYMEN (13) compared the action of solutions of various acids on soils whose manurial history was known and they state in conclusion :- "of the acids examined the one per cent citric acid gives results most in agreement with the recorded history of the soil, although there is evidence that the same interpretation cannot be put on the results obtained from all types of soil". KÖNIG and HASENBÄUMER (19) have also used a one per cent citric acid method which differs from Dyer's original method in the time of extraction.

A.E.MITSCHERLICH (26) has used a saturated solution of $CO_2$ /

$CO_2$ in water to estimate the available potash since this, in his opinion, represents the conditions under which the plants obtain their supply of nutrient. This extraction method is no longer used by Mitscherlich as a result of the development of his pot culture method which will be described later.

NĚMEC (30) has determined the potash in aqueous soil extracts and has suggested that the values so obtained give an indication of the necessity for potash manuring. Water extraction methods have been extensively used in the United States and references to the literature on the subject are given by G.R.STEWART (44) in a paper dealing with the effect of crop growth on the composition of the extract and its seasonal variation.

(b) Neubauer's Seedling Method.

H. NEUBAUER (31) has made use of plants themselves to extract the mineral nutrients from the soil with the idea of obtaining a definite estimate of the quantity of available or 'root-soluble' nutrients. The method was developed as a result of experiments on the absorption of potash and phosphoric acid by young seedlings. It is assumed that if a relatively large number of seedlings are grown in a small quantity of soil there will be practically complete transference of the nutrients from the soil to the roots of the seedlings. The practical procedure consists in growing 100 rye seedlings in small glass pots, with a surface area of 100 sq. cms. and 7 cm. in depth, in /

in a mixture of 100 gms. soil and 300 gms. pure quartz sand for a period of 18 days, which was found to give the maximum extraction. At the end of this period the roots and shoots are separated from the soil and sand by washing and the potash and phosphoric acid determined by chemical analysis of the ignited plant residues.

In the case of potash from 0 up to 50 milligrams of $K_2O$ may be extracted from the soil by the seedlings.

Neubauer has calculated what he calls 'limit values' from which it is possible to judge the manurial requirement of the soil. The 'limit values' are considered to represent the optimum nutrient concentration and above which it is considered the soils are sufficiently supplied with the particular nutrient and can be expected to give a high yield of crop without further manuring. The limit values are based on the average chemical composition of the various crops and the fraction of 'root-soluble' nutrient which is supposed to be available to the plant under practical conditions. Further particulars of the technique of the method and a list of limit values are given by NEUBAUER (32) in a recent publication. ROEMER (38) has determined limit values from an extensive series of field experiments and in general good agreement with the calculated values was obtained.

The Neubauer method has attracted a great deal of attention in Germany. Since its introduction in 1923 over 100 papers have appeared in the various German Agricultural Journals containing /

containing criticisms of the method either on theoretical or practical grounds, and giving the results of numerous comparisons with field experiments. The quantities of $K_2O$ and $P_2O_5$ extracted by the seedlings are undoubtedly dependent on external conditions and careful standardisation is necessary before reproducible results can be obtained. The variety of rye seed, grain size, water content of soil-sand mixture, temperature, and light, may influence the results, and the previous treatment of the soil has also a marked effect on the values obtained. A good description of the observations made on these points is given by S. GERICKE (12). Later references may be obtained in papers by F.W.WACKER (45), ? Lemmer or ? 23
LINKERMANN (21), K. SCHUMANN (41) and in Neubauer's second article.

K. BAMBERG (2) has shown that for weakly acid, neutral or slightly alkaline soils of Lettland there is a correlation between the exchangeable $K_2O$ and the Neubauer $K_2O$, the latter varying from 75% - 95% of the former. More recently he has found that the percentage extraction is less in more acid soils, being in some cases only 20% or less of the exchangeable $K_2O$. A. GEHRING (10) has arrived at somewhat similar conclusions. This relationship between the exchangeable and Neubauer $K_2O$ will be considered later, when the results obtained with some Scottish soils are included.

(c) Mitscherlich's Plant Growth Method.

MITSCHERLICH (27) has developed a method of soil examination /

examination which is based on a fundamental theory of plant growth. LIEBIG (22) was one of the first to attempt to formulate a law of plant growth and his "Law of the Minimum" stated that the fertility of a field was governed by that essential constituent of plant nutrition which was present in the soil in the relatively smallest quantity. This was later supplemented by Liebscher's "Law of the Optimum" which stated that the plant can make the greater use of the minimum factor the more the others are present in optimum. Mitscherlich's "Law of the Physiological Relationships" goes further than this and states that the plant yield can be increased by each single growth factor even when it is not present in minimum and so long as it is not present in optimum; and that each growth factor can effect the yield quite independently of all others. The magnitude of the effect produced on the yield by any factor is given by Mitscherlich's "Law of the effect of the Growth-factors" which states that the increase in yield due to a given increase in a growth factor is proportional to the decrement from the maximum yield which could be obtained by increasing that particular factor. This is expressed mathematically as follows :-

$$\frac{dy}{dx} = C(A - y) \qquad (1)$$

where $\frac{dy}{dx}$ is the rate of increase in yield produced by an increase x in the value of the factor, while A is the value of the maximum yield obtainable by increasing that factor under the given conditions and C is the proportionality constant /

constant or "Wirkungsfaktor". On integration equation I becomes -

$$\log_e (A - y) = K - cx \text{ - - - - - - - - - } (2)$$

Since the yield y must be zero when z = o, we get $\log_e A = K$ on putting x = o and substituting this value of K in equation 2 we get -

$$\log_e (A - y) = \log_e A - cx \text{ - - - - - } (3)$$

or on solving for y -

$$y = A\left(1 - e^{-cx}\right)$$

This equation expresses the effect on the yield produced by a single growth factor and BAULE (3) has given the equation a general form applicable to all the growth factors. His equation is -

$$y = A(1 - e^{-cx})(1 - e^{-c_1 x_1}) \ldots\ldots (1 - e^{-c_n x_n})$$

where $x$, $x_1$, .... $x_n$ represent the quantities of the factors present and $c$, $c_1$, .... $c_n$ are their respective proportionality constants or "Wirkungsfaktoren". Mitscherlich defines a "growth-factor" as "any physical or chemical, or, if one likes, any biological factor which can exert an influence on the plant yield". He states that the "Wirkungsfaktor" for any particular growth-factor is a constant, independent of the value of the maximum yield A and independent of all other growth factors. He has determined experimentally, both by pot experiments and field experiments, the values of the "Wirkungsfaktoren" for the nutrients, potash, phosphoric acid and nitrogen.

When considering the effect of the addition of a fertiliser to /

to a soil which already contains a certain quantity b of the nutrient in an available condition, equation 3 becomes -

$$\log(A-y) = \log_e A - c(x+b)$$

It follows from the equation that b can be determined if we know the value of the corresponding Wirkungsfaktor c and the value of A, the maximum yield. A can be determined experimentally by pot experiments for potash and phosphoric acid and hence the quantities of these fertilisers which are present in the soil in an available condition can be calculated.

Mitscherlich's method has, however, been subjected to considerable criticism. His method of calculating the value of c from his experimental results has been objected to by FRÖHLICH (8), while his whole treatment of the subject has been criticised by BRIGGS (6). LEMMERMANN (21) and GERLACH (11) have published criticisms of Mitscherlich's work and conclude that the values of the "Wirkungsfaktoren" for nitrogen and phosphoric acid are not constant. Lemmermann's experimental results when carefully examined, however, do not support his conclusions, and it is doubtful if the accuracy of his field trials is such that reliance can be placed on the values of c calculated from the figures. In his pot experiments his curves are evidently not logarithmic and therefore of little value for the calculation of the constants in a logarithmic equation. This variation from the true logarithmic curve is to be expected when two factors have been varied instead of the one under examination. RIPPEL (36) has found variation in the value /

value of c for potash and as his experiments have been very carefully carried out the results are presumably correct. Mitscherlich's reply to Rippel's results is given in a recent paper (28) in which he introduces a modification of his original equation to account for the fact that applications of manures beyond a certain limit produce a decrease in the maximum yield which can be obtained. The new equation expressing the relationship between the yield and a single growth factor is -

$$y = A(1 - 10^{-cx}).10^{-kx^2}$$

where k represents a harmful or 'injury' factor (Schädigungsfaktor) Mitscherlich's experiments have shown that this factor is dependent on the nature of the manure, the buffering and water-holding capacity of the soil, and changes in the climatic growing conditions. For example this factor seems to be greater for ammonium sulphate and for superphosphate in sand cultures than in soil cultures.

While it seems that the logarithmic law applies within the limits of experimental error when only one factor is varied it can be shown that other equations can be obtained which fit the facts again within the limits of experimental error. PFEIFFER and FRÖHLICH (8) suggested that a parabola of the general form

$$y = ax^2 + bx + c$$

would be just as accurate. A similar formula was suggested by Briggs. NIKLAS and MILLER (33) showed that certain of Mitscherlich's results are expressible by a parabolic equation, and that the fit was just as good as with the logarithmic law. BALMUKAND /

BALMUKAND (1) has made a valuable contribution to the subject and examines in detail the theoretical requirements of any yield factor law. He shows that Mitscherlich's equations do not correctly express the results from some Rothamsted experiments, and has tested by critical statistical methods the applicability of a Resistance Formula to the results of several two-factor experiments. The Resistance Formula requires that $\frac{1}{y} - \frac{1}{y'}$, the difference of reciprocals of yields should be independent of the influence of other factors instead of the ratio $\frac{y'}{y}$ behaving as such as would be required by Mitscherlich's law. It is shown that the yield is expressible by the general formula -

$$\frac{1}{y} = F(N) + F'(K) + F''(P) \ldots\ldots + C$$

and that the expressions F(N) and F (K) are well represented by the form $\frac{a_n}{n + N}$ and $\frac{a_k}{k + K}$ where N and K are the nutrients added to the soil, while $a_n$ and $a_k$ are constants for the several types of manures. The parameters of the Resistance Formula are capable of direct interpretation as physical quantities; for each nutrient there are two constants; one represents the importance of that particular nutrient to the crop concerned and the other is a measure of the amount of nutrient available to the plant in the unmanured soil. No very extensive proof of the Formulae is given by Balmukand, but it appears to be worthy of serious consideration.

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## II. EXPERIMENTAL.

The experimental work can be divided into two parts -
(1) a general examination of the potash content of some typical East of Scotland soils by several of the standard methods previously described; and
(2) a detailed examination of six soils, by the Mitscherlich and Neubauer methods, to test the conclusions arrived at from the results of the general examination.

### PART I.

### OCCURRENCE OF POTASSIUM IN SOME SCOTTISH SOILS AND THE 'AVAILABILITY' AS MEASURED BY DYER'S METHOD IN RELATION TO THE EXCHANGEABLE POTASSIUM.

The methods used included Dyer's citric acid extraction, the standard English method of extraction with hot concentrated hydrochloric acid, and the determination of the exchangeable potash. A few determinations of the total mineral potash have been made in order to obtain a comparison with the hydrochloric acid method. Some soils have been examined by Neubauer's seedling method and the values obtained compared with exchangeable potash content.

(a) Experimental methods employed.

The total mineral potash was determined by the Lawrence-Smith method - 0.5 gms. of the finely powdered soil were heated in a platinum crucible with a mixture of ammonium chloride /

chloride and calcium carbonate and the soluble chlorides extracted from the residue with hot water and the potash determined in the resulting solution.

The HCl soluble potash was determined by the standard English method - 20 gms. of soil were treated with 70 ccs. constant boiling point hydrochloric acid for 48 hours on the water bath and the potash determined in an aliquot portion of the filtrate.

The citric soluble potash was determined by Dyer's original method - 200 gms. soil were treated for 7 days with 2,000 ccs. 1 per cent citric acid solution with frequent shaking and the potash determined in 500 ccs. of the filtrate. The exchangeable potash was determined by extracting 25 gms. of soil with a normal solution of ammonium chloride until 500 ccs. of filtrate were obtained.

The potassium was determined in all the extracts by the volumetric cobaltinitrite method of MORRIS (29). This method has been found to be very convenient and accurate for the small quantities of potash dealt with. In some preliminary experiments using the perchloric acid method the precipitate of potassium perchlorate was found invariably to contain traces of sulphate.

(b) Results of Analyses.

Table I contains a list of the soils examined together with the depths to which they were sampled and brief geological /

geological and cultivation notes. In those cases where a complete profile was available the individual layers were analysed with the exception that a purely peaty or organic layer was ignored. The letters (a) (b) and (c) etc. merely refer to successive layers and not to the A, B, and C horizons. The soils were all air dried and the fraction passing the 3 m.m. sieve used for the analyses.

The results of the determination of the HCl-soluble, citric acid soluble, and exchangeable potash are given in Table I, and the values obtained for the total mineral potash are given in Table II. The figures given are the means of at least duplicate determinations.

TABLE I. /

## T A B L E I.

| LOCATION OF SOIL SAMPLE AND NOTES ON GEOLOGY AND CULTIVATION. | SOIL NO. | DEPTH | pH |
|---|---|---|---|
| BOGHALL, MIDLOTHIAN. Cultivated Alluvial flat over Basalt. | 548a | 0-6" | 6.37 |
| | b | 6-14" | 6.87 |
| | c | 14-26" | 6.78 |
| | d | 26-48" | 6.92 |
| | e | 48-60" | 6.95 |
| BOGHALL, MIDLOTHIAN. Cultivated Alluvium over Basalt. | 169a | 0-9" | 6.07 |
| | b | 9-18" | 6.19 |
| BOLSHAM, ANGUS. Pine wood. Thin Boulder Clay over Andesite. | 843b | 4-11" | 4.63 |
| | c | 11-19" | 4.71 |
| | d | 19-39" | 5.84 |
| BOGHALL, MIDLOTHIAN. Cultivated Glacial Sand & Gravel. | 509a | 0-9" | 5.92 |
| | b | 9-18" | 6.26 |
| CRAIBSTONE, ABERDEENSHIRE. Cultivated Boulder Clay over Granite. | 399a | 0-9" | 5.59 |
| INSCH, ABERDEENSHIRE. Cultivated thin Boulder Clay over Norite. | 398a | 0-9" | 5.94 |
| HUMBIE, EAST LOTHIAN. Cultivated Glacial Sand and Gravel over Sandstone. | 672a | 0-9" | 6.78 |
| | b | 9-24" | 7.08 |
| OLD FARGIE, PERTHSHIRE. Uncultivated Grass. Thin Soil over Andesite. | 593a | 0-6" | 5.62 |
| | b | 6-20" | 5.81 |
| POLMONT, STIRLINGSHIRE. Good Grass, seldom ploughed. Carse Soil (Alluvium). | 589a | 0-8" | 5.26 |
| | b | 8-20" | 6.24 |
| | c | 20-48" | 7.68 |
| | d | 48-72" | 7.73 |
| GLENFARG, PERTHSHIRE. Grass in open wood, uncultivated. Thin Soil over Andesite. | 592a | 0-7" | 5.32 |
| | b | 10-24" | 5.36 |
| ALVA, CLACKMANNANSHIRE. Cultivated but usually under Grass. Alluvial flat. | 591a | 0-8" | 5.90 |
| | b | 8-20" | 5.32 |
| | c | 20-40" | 5.53 |
| DUNBAR, EAST LOTHIAN. Cultivated. Thin Boulder Clay. | 587a | 0-8" | 6.70 |
| | b | 8-20" | 7.37 |
| | c | 20-36" | 7.07 |
| BRIDGE OF EARN, PERTHSHIRE. Grass at edge of stream. Carse Soil (Alluvium). | 590a | 0-7" | 5.79 |
| | b | 7-24" | 4.98 |
| | c | 24-48" | 4.86 |
| | d | 48-72" | 2.97 |

TABLE I. (Contd).

| SOIL NO. | HCl SOLUBLE $K_2O$. | CITRIC SOLUBLE $K_2O$ | EXCHANGEABLE $K_2O$ |
|---|---|---|---|
| 548a | 0.213% | .0025% | .0051% |
| b | 0.265 | .0025 | .0048 |
| c | 0.331 | .0028 | .0055 |
| d | 0.261 | .0029 | .0044 |
| e | 0.334 | .0014 | .0036 |
| 169a | 0.265 | .0032 | .0058 |
| b | 0.250 | .0020 | .0048 |
| 843b | 0.290 | .0031 | .0065 |
| c | 0.482 | .0026 | .0037 |
| d | 0.616 | .0032 | .0060 |
| 509a | 0.251 | .0038 | .0066 |
| b | 0.260 | .0023 | .0050 |
| 399a | 0.490 | .0035 | .0088 |
| 398a | 0.524 | .0053 | .0107 |
| 672a | 0.191 | .0062 | .0116 |
| b | 0.182 | .0029 | .0056 |
| 593a | 0.310 | .0074 | .0189 |
| b | 0.317 | .0021 | .0080 |
| 589a | 0.742 | .0102 | .0195 |
| b | 0.773 | .0084 | .0192 |
| c | 0.711 | .0146 | .0246 |
| d | 0.670 | .0402 | .0563 |
| 592a | 1.01 | .0095 | .0212 |
| b | 0.374 | .0013 | .0049 |
| 591a | 0.136 | .0124 | .0217 |
| b | 0.994 | .0129 | .0228 |
| c | 1.12 | .0144 | .0254 |
| 587a | 0.342 | .0145 | .0230 |
| b | 0.374 | .0046 | .0062 |
| c | 0.673 | .0047 | .0059 |
| 590a | 0.369 | .0285 | .0490 |
| b | 0.953 | .0062 | .0152 |
| c | 1.09 | .0066 | .0136 |
| d | 0.833 | .0015 | .0050 |

## TABLE II.

| | | | | | | |
|---|---|---|---|---|---|---|
| SOIL NO. ........... | 589a | 590a | 591a | 592a | 593a | 548a |
| TOTAL MINERAL $K_2O$ .. | 2.51% | 3.00% | 2.13% | 1.87% | 1.51% | 1.22% |
| HCl SOLUBLE $K_2O$ .... | 0.742 | 0.369 | 0.136 | 1.01 | 0.310 | 0.213 |

(c) Discussion of Results.

All the soils examined show an acid reaction in the surface layer, but soils 672, 589 and 587 become alkaline in the lower layers. The basal material of soil 590 has the abnormally low pH of 2.97 and the soil was found to contain considerable quantities of water extractable aluminium sulphate. With two exceptions, soils 590 and 591, there is a decrease in acidity with increase in depth of sampling.

In the six soils examined the total mineral potash lies between 1.22 and 3.00% with an average value of 2.04%. The three alluvial soils - 589, 590 and 591 - are much richer in potash than the three drift soils - 592, 593 and 548. The relation to the HCl-soluble potash shows no kind of regularity, the percentage HCl-soluble to total varying from 6.6% to 54%.

ROBINSON, STEINKOENIG and FRY (37) have given the results of the total analyses of 34 American soils of widely different types and representative of considerable areas. The values of the potash range from 0.05% to 3.96% with a mean value of 1.00%. RUSSELL (39) has given the results of the analyses of 11 South of England soils in which the potash ranges from 0.30% to 1.44% with /

with a mean value of 0.65%. These figures would indicate that the Scottish soils examined possess comparatively large reserves of potash. This is in agreement with the evidence obtained from the mineralogical analyses of similar soils carried out by HENDRICK and NEWLANDS (16) who found that the Scottish soils contained larger quantities of unweathered mineral fragments than the South of England soils examined by them.

The quantities of potash soluble in hot strong hydrochloric acid vary from 0.14% to 1.21% of the air-dry soil and the average value for all the soils is 0.500% and for the surface soils 0.395%. In the profile samples there is generally an increase in soluble potash with increase in depth of soil, with one marked exception in soil No. 592. In soils 590 and 548 there is an indication of a layer of accumulation, but the profile of soil 589 shows no accumulation and there is a slight decrease in solubility in the lower layers. The Carse soils are seen to be the richest in HCl-soluble potash. Soil 591 shows a remarkable increase in solubility with depth varying from the lowest to the highest value obtained in the series. This variation is not paralleled in the case of the citric soluble or exchangeable potash in this soil.

The quantities of potash extracted by the 1% citric acid solution show a much greater range of variation than do the quantities extracted by concentrated hydrochloric acid /

acid, varying from .0013% to .0402% with an average value of .0074%. For the surface soils the values lie between .0025% and .0285% with a mean value of .0086%. With but a few exceptions the quantities extracted and their ratio to the HCl-soluble potash decrease with increase in depth of soil. The most definite exception is soil No. 589 which contains nearly four times as much citric soluble $K_2O$ in the basal material as in the surface soil. The proportion of the HCl-soluble potash extracted by the citric acid also varies considerably, the quantities extracted varying from 0.18 to 7.7% of the former. Discussing the relationship between the two methods of analysis, RUSSELL (40) states that "the available potash shows no kind of regularity but varies between 5 and 50% of the quantity extracted by strong acids". In the Scottish soils examined this proportion is very much lower but there is also no regularity when compared with the HCl-soluble potash. The lower proportion may be due to the higher average value of the HCl-soluble potash combined with a lower value of the citric soluble or "available" potash, Russell gives the average value of the available potash in eight South of England soils as .017% which is practically twice the value for the Scottish soils.

The values obtained for the exchangeable potash vary from 0.0036% to 0.0563% with an average value for the samples from all the layers of 0.0135%. The average value for the surface soils is slightly higher, being 0.0161%. There is the /

the same general decrease in quantity with increase in depth of soil as was observed in the case of the citric soluble potash. On comparing the potash present in the exchangeable form with that soluble in hydrochloric acid, the proportion is seen to vary considerably, ranging from 0.56 to 15.5% of the latter. When a comparison is made between the exchangeable and citric soluble potash a fairly close relationship is seen to exist between the two quantities, the ratio of citric soluble to exchangeable varying from 26 to 79%, with an average value of 52%.

The product moment correlation coefficient between the two series, calculated in the usual manner, is found to be $r = +.98$. In order to test the significance of this coefficient the method given by FISHER (9) was employed. For a coefficient of this value obtained from 34 samples $t = \frac{r}{\sqrt{1-r^2}} \sqrt{n-2} = 26.9$ For a probability P = .01 that the two series are not correlated 't' should be about 2.75. Since P decreases with increase in 't' it is evident that there is an extremely small probability that the two series are not correlated.

This relationship is to be expected if we consider the citric acid extraction to be a case of partial base exchange. As the citric acid extract has a pH value of about 2.5 it cannot be expected to have much solvent action on the soil minerals, and if it is assumed that the action of the acid does not entirely destroy the power possessed by the soil of adsorbing bases it is evident that there must be a state of equilibrium /

equilibrium in any such solution in contact with the soil. In the ordinary methods for determining the exchangeable bases this equilibrium is disturbed by making repeated extractions with fresh solvent until the quantity of potash in the extracts becomes vanishingly small.

Wiegner has shown that there is a dynamic equilibrium in the solution in contact with an adsorbing colloid, and this equilibrium is independent of concentration but dependent on the ionic ratio of ions in the solution. In the case of the citric acid extract the potash extracted would, therefore, depend on the cationic ratios in the extract, and on the nature of the undecomposed adsorbing complex. These two factors would naturally vary with each soil and would account for the variations observed between different soils. The fact that the quantity of potash extracted by the citric acid was always much less than the exchangeable content, indicates that there could have been very little, if any, potash liberated by the citric acid apart from that previously existing in the exchangeable form.

The three soils Nos. 548, 169 and 509 from the Experimental Farm of the Edinburgh and East of Scotland College of Agriculture, Boghall, Midlothian, are very similar, being comparatively low in HCl-soluble and very low in citric soluble and exchangeable potash. The other glacial sand and gravel - No. 672 - is also very low in HCl-soluble potash but slightly richer in citric soluble and exchangeable. Soils 592 /

592 and 593 are very similar in origin, being thin soils over andesite and probably residual. The citric soluble and the exchangeable figures are alike but there is quite a large difference in HCl-soluble potash, although the total mineral values for these soils are fairly similar. Soil No. 843, also over andesite but with thin drift, is the only soil from a wood and the values of the citric soluble and exchangeable potash are much lower than the other andesite samples, although the HCl-soluble content is similar to soil 593. The Aberdeenshire soils - Nos. 398 and 399 - are derived from boulder clay over granite and norite respectively. The analytical results are similar, both soils containing moderately large quantities of HCl-soluble potash while the citric soluble and exchangeable values are comparatively low. The two Carse soils (alluvium) are among the richest of the soils examined, soil 590 containing twice as much exchangeable potash as any other examined. This soil has also the very high value of 3.00% total mineral potash. It may be noted that of the last eight soils six are either permanently or usually under grass vegetation, but it is impossible from the above data to draw definite conclusions regarding the effect of cultivation on the potash content of the soil.

The results obtained from thirteen surface soils and one basal soil when examined by Neubauer's seedling method are given in Table III, together with the corresponding values of the exchangeable potash. Six of the soils are from Boghall Farm /

Farm, Midlothian, and of the others, four are from Aberdeenshire, two from Angus and one from Stirlingshire.

TABLE III.

| SOIL NO. | LOCATION | 'NEUBAUER' $K_2O$ | EXCHANGEABLE $K_2O$ |
|---|---|---|---|
| 1117 | Boghall Farm, Midlothian. | .0073% | .0098% |
| 1118 | do. | .0053 | .0081 |
| 1119 | do. | .0066 | .0097 |
| 1120 | do. | .0056 | .0082 |
| 976 | do. | .0081 | .0098 |
| 1061 | do. | .0061 | .0114 |
| 589a | Near Polmont, Stirlingshire. | .0129 | .0195 |
| 589d (basal) | do. | .0424 | .0563 |
| 1006 | Silverhill, Aberdeenshire. | .0070 | .0085 |
| 1007 | do. | .0311 | .0341 |
| 1008 | do. | .0078 | .0102 |
| 1009 | do. | .0057 | .0065 |
| 1059 | Inverkeilor, Angus. | .0152 | .0206 |
| 1060 | Brechin, Angus. | .0258 | .0317 |

Neubauer's average "limit-value" for the potash extracted by the seedlings is 24 mgs. per 100 gms. soil or a content of 0.0240%. On this basis the Boghall soils with about 5 to 8 mgs. would appear to be very deficient in available /

available potash. Soils 1007 and 1060 are the only surface soils sufficiently supplied with potash and the basal soil 589d at a depth of 4 to 6 feet is seen to be easily the richest of the soils examined.

When the Neubauer values are compared with the values of the exchangeable potash there is evidence of a correlation between the two quantities. The ratio of "Neubauer" to exchangeable varies from 53 to 91% with a mean value of about 74%. This is somewhat higher than the mean value of 52% obtained from similar soils for the citric acid/exchangeable ratio, and emphasised the power of theyoung seedlings to absorb available potash from the soil. The correlation coefficient obtained between the values of "Neubauer" $K_2O$ and exchangeable $K_2O$ is $r = + .989$. From this we obtain a value of $t = 22.94$. For a probability $P = .01$ the value of $t$ should be about 3.05 and the extremely high value obtained indicates a correspondingly high probability that the two values are correlated.

HASENBÄUMER and BULKS (15) describe some experiments in which quantities of $K_2O$ in the form of potassium chloride were added to a soil and the mixture subsequently analysed by their 1% citric acid method and by the seedling method. For three soils the percentage extractions by the citric acid solution were 80, 61, and 67% (Mean 69%) and by the seedling method 76, 78, and 91% (Mean 82%). While the citric acid figures are not strictly comparable with the present data owing to the /

the different technique, the figures for the seedling extraction are interesting and suggest that practically all the potash existing in a soil in the exchangeable form must be considered to be available to the plant, although the quantity available at any particular time is in all probability governed by several factors.

SVEN ODÉN (34) has published recently a very interesting paper containing the results of an exhaustive examination by means of electrodialyses of some Swedish and Dutch soils together with the results of experiments on the buffering capacity of soils in relation to their content of exchangeable bases. In order to demonstrate the importance of the replaceable ions in plant nutrition he extracted all the replaceable ions from a rich garden soil by means of electrodialyses; the dialysate was then added to pure quartz sand and oats were grown on the sand and also on the extracted soil. The oats grown in the soil were unable to develop and it was shown that a considerable part of the mineral content of the seed was given off to the soil which in this way became more saturated with bases. Odén concludes that "this demonstrates clearly that the growing plants obtain their nutritive salt ions only from the swarm of replaceable ions surrounding the soil particles and cannot dissolve or utilise any food from the soil minerals. The maximum amount of available salts in the soil is, therefore, identical with the replaceable ions".

<u>P A R T 2.</u> /

# P A R T 2.

## DETAILED EXAMINATION OF SIX SOIL SAMPLES.

The most important result of the general examination of the potash content in some Scottish soils was the indication of the importance of the content of replaceable or exchangeable potassium in relation to the availability of this nutrient for plant growth. This relationship has been examined further in six soil samples from arable land in the East and South East of Scotland. Through the assistance of Dr. W. G. Ogg of the Edinburgh and East of Scotland College of Agriculture, the necessary facilities were obtained to conduct Mitscherlich's pot-culture method on these soils. The Neubauer seedling method values were also obtained and a complete determination made of the important chemical properties of those soils.

### (a) Soils examined and their main chemical characteristics.

The soil samples were taken from the East of Scotland area, three being from Berwickshire, and one each from Selkirkshire, Haddingtonshire and Midlothian. The results of the analyses carried out on these soils are given in Table IV.

T A B L E IV. /

TABLE IV.

| LOCATION | SOIL NO. | pH | %AGE $H_2O$ | LOSS ON IGNITION | MOISTURE AT "STICKY-POINT". | HCl-SOLUBLE $K_2O$ | EXCHANGEABLE CaO | | EXCHANGEABLE $K_2O$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | %AGE | MGM.EQUIV. | %AGE | MGM.EQUIV. |
| BOGHALL, MIDLOTHIAN. | 1138 | 5.63 | 2.13 | 7.27% | 28.9% | 0.215% | 0.320 | 11.4 | 0.0113 | 0.240 |
| LINDEAN, SELKIRKSHIRE. | 1139 | 5.96 | 2.11 | 7.73 | 34.3 | 1.105 | 0.257 | 9.2 | 0.0309 | 0.655 |
| HARPERDEAN, HADDINGTONSHIRE. | 1140 | 7.18 | 2.27 | 7.07 | 29.1 | 0.265 | 0.192 | 6.8 | 0.0175 | 0.371 |
| SUNWICK, BERWICKSHIRE. | 1141 | 5.30 | 2.48 | 8.38 | 38.0 | 0.674 | 0.295 | 10.5 | 0.0317 | 0.672 |
| BLACKADDER MOUNT, BERWICKSHIRE. | 1142 | 6.85 | 2.19 | 6.44 | 32.3 | 0.796 | 0.331 | 11.8 | 0.0326 | 0.691 |
| KAIMES EAST MAINS, BERWICKSHIRE. | 1143 | 6.40 | 2.64 | 7.22 | 32.3 | 0.342 | 0.343 | 12.2 | 0.0079 | 0.167 |

The range of pH values is normal for this area, and the "Moisture at Sticky-point" values, which are a rough measure of the textural characteristics, are fairly uniform and indicate medium to slightly heavy loams. The exchangeable base contents are very similar to those given by SMITH (43) with the exception that the exchangeable potash values are somewhat higher in the present series of soils.

(b) Mitscherlich Results.

It was decided to examine the soils by Mitscherlich's pot method using the technique developed by him and assuming the correctness of the value of the "effect-factor" which Mitscherlich has deduced from his extensive experiments at Königsberg.

During the theoretical discussion of Mitscherlich's laws it was shown (p.12) that the equation connecting the yield and concentration of manurial factor could be expressed by -

$$\log_e (A - y) = \log_e A - cx$$

or

$$\log (A - y) = \log A - c_1 x \qquad (4)$$

where $C_1 = 0 \cdot 4343\, C$

This equation shows the relation between the yield $y$ produced by a concentration $x$ and the maximum yield $A$ which can be obtained from that factor, while $C$ is the "Wirkungsfaktor" or Effect-factor.

If $x$ represents the concentration of potash in the soil /

soil it is evident that, given the value of $c$ or $c_1$, $x$ can be determined if we can find by experiment the values of $A$ and $y$. If the manurial concentrations are expressed in gms. per pot Mitscherlich gives the value of $c_1$ for potash to be 3.02 gms. $K_2O$ per pot.

In his soil examination work Mitscherlich uses oats as the experimental plant. A series of pots are filled with a 1 to 1 mixture of soil and sand, to which have been added the appropriate manurial dressings, and 35 oat plants are grown to maturity under carefully controlled conditions. The sand is added, partly to act as a dilutant, and partly to improve the physical condition of the soil. When the oats have ripened, the straw and grain are harvested from each pot, dried in an air oven at 105°C, and weighed.

For the determination of 'A' a 'complete' manurial dressing is given consisting of 3.0 gms. $NH_4NO_3$, 6.5 gms. 18.5% Superphosphate and 3.0 gms. $K_2SO_4$ per pot. Those salts are added to the soil-sand mixture as solutions of appropriate concentrations and thoroughly mixed in before the pots are filled. For the determination of 'y' the $K_2SO_4$ is omitted from the manurial dressing and the yield is, therefore, governed by the concentration of $K_2O$ in the soil. In order that some measure of the error attached to these determinations may be obtained a series of four replicates is made for each treatment.

A series of eight pots are, therefore, required for each /

each soil sample when the potash concentration is determined, four pots receiving a 'complete' manurial dressing, and four pots the same dressing with the omission of potash.

In the present experiment the pots were sown with Victory Oats on the 22nd April 1929 and harvested on the 6th September 1929. The yield of dry matter from each pot is given in Table V, together with the mean valuesof the yields from each treatment and the corresponding Standard Errors calculated from the equation Standard Error = $\sqrt{\frac{\Sigma d^2}{n(n-1)}}$

TABLE V.

| SOIL NO. | 1138 | 1139 | 1140 | 1141 | 1142 | 1143 |
|---|---|---|---|---|---|---|
| | gms. | gms. | gms. | gms. | gms. | gms. |
| Yields with | 110.7 | 36.0 | 98.3 | 95.7 | 83.6 | 96.2 |
| 'complete' | 98.3 | 32.6 | 93.6 | 103.1 | 91.3 | 99.7 |
| | 97.6 | 28.0 | 99.5 | 97.6 | 90.2 | 90.1 |
| Manure = A. | 101.9 | 31.8 | 103.3 | 94.2 | 90.6 | - |
| Mean Values - | 99.6 | 32.1 | 98.7 | 97.6 | 88.9 | 95.3 |
| Standard Error | ±1.0 | ±1.6 | ±2.0 | ±1.9 | ±1.8 | ±3.1 |
| Yields with- | 71.5 | 31.0 | 90.6 | 70.1 | 90.8 | 50.3 |
| out potash | 71.8 | 33.6 | 93.1 | 75.2 | 96.4 | 50.6 |
| | 74.5 | 31.1 | 85.7 | 80.1 | 86.7 | 48.2 |
| manure = y. | 71.8 | - | 90.2 | 75.0 | 91.4 | - |
| Mean Values - | 72.4 | 31.9 | 89.9 | 75.1 | 88.8 | 49.7 |
| Standard Error | ±0.7 | ±0.7 | ±1.5 | ±2.0 | ±1.3 | ±0.7 |

In the case of soil No. 1139 the figures given refer to the straw yields only. The oats on this soil ripened more rapidly than /

than in the other series, and suffered some loss of grain owing to wind action before the plants were harvested. Since Mitscherlich claims that his equation applies to yield of straw as well as to yield of straw plus grain it was considered that a more accurate result would be obtained in this case from the straw yields. In the case of the other five samples it will be noticed that, with the single exception of soil No. 1142, the maximum yields are the same within the limits of experimental error.

The various stages in the calculation of the potash concentration in each soil sample are given in Table VI. The weight of $K_2O$ in gms. per pot is calculated from a modification of equation No. 4 on page 32. If y is expressed as a percentage of A, equation 4 becomes -

$$\text{Log}\,(100 - y) = \text{Log}\,100 - c_1 x$$

Since $c_1$ = 3.02 gms. per pot

$$x = \frac{\log 100 - \log (100 - y)}{3 \cdot 02}$$

The weight of dry soil per pot was known so that the weight of $K_2O$ per 100 gms. dry soil could be calculated.

T A B L E VI. /

T A B L E VI.

| SOIL No. | YIELDS IN GMS. PER POT | | y as % of A | $K_2O$ IN GMS.PER POT = x. | WEIGHT DRY SOIL IN POT. | $K_2O$ PER 100 GMS.DRY SOIL. |
|---|---|---|---|---|---|---|
| | A | y | | | | |
| 1138 | 99.6 | 72.4 | 72.7 | 0.187 | 2850 gms. | .0066 |
| 1139 | * 32.1 | 31.9 | 99.4 | 0.736 | 3110 | .0237 |
| 1140 | 98.7 | 89.9 | 91.1 | 0.348 | 3020 | .0115 |
| 1141 | 97.6 | 75.1 | 76.9 | 0.211 | 2580 | .0082 |
| 1142 | 88.9 | 88.8 | 99.9 | 0.993 | 2780 | .0357 |
| 1143 | 95.3 | 49.7 | 52.2 | 0.106 | 2820 | .0038 |

* Yield of straw only.

(c) Mitscherlich Results in relation to Neubauer and Exchangeable Potash Values.

In Table VII the content of exchangeable potash in the six soils together with the results of the Neubauer seedling analyses are reported for comparison with the pot experiment results. The figures given represent gms. $K_2O$ per 100 gms. dry soil.

T A B L E VII.

| SOIL NO. | 1138 | 1139 | 1140 | 1141 | 1142 | 1143 |
|---|---|---|---|---|---|---|
| MITSCHERLICH $K_2O$ ... | .0066 | .0237 | .0115 | .0082 | .0357 | .0038 |
| NEUBAUER $K_2O$ ....... | .0104 | .0287 | .0161 | .0243 | .0257 | .0053 |
| EXCHANGEABLE $K_2O$ ... | .0113 | .0309 | .0175 | .0317 | .0326 | .0079 |

It will be noticed that the Neubauer values are in every case less than the exchangeable $K_2O$, and with one exception, soil No. 1142, greater than the values deduced from the pot experiments. The relative proportionsof the mean values are -

Exchangeable - 100; Neubauer - 84; Mitscherlich - 68.

The significant correlation previously observed between the exchangeable and Neubauer values is again obtained. For this series of six soils the correlative coefficient 'r' = + .976 and is definitely significant. This confirmatory evidence supports the conclusion that the seedlings during the short growing period in the Neubauer estimation absorb potash only from /.

from the supply existing as a constituent of the exchangeable base content of the soil.

The correlation coefficient between the Mitscherlich and Neubauer values, and between the Mitscherlich and exchangeable values, are very similar, 'r' being equal to + .735 and + .721 respectively. While this is a high coefficient value the correlation cannot be considered to be absolutely significant, the probability against significance being about 0.1 in each case. This uncertainty is due to the small number of comparisons necessitating a very high co-efficient for definite significance, and may also be due to the large experimental error associated with the Mitscherlich values. It is unfortunate that the six soils under examination, although chosen at random, should be relatively rich in potash. This is particularly the case with regard to soils Nos. 1139, 1140 and 1142, for which the yield without addition of potash represented 90% or more of the maximum yield. The logarithmic nature of the relationship between 'y' and 'x' results in a large variation in the value of 'x' for a small variation in 'y' when 'y' represents 90% or more of 'A'. Although the standard errors of the yields from the pot experiments are only about 2% on the average this gives a comparatively large variation in the determination of 'x', and there is therefore a relatively greater error attached to the Mitscherlich values than to the Neubauer or exchangeable values.

It is significant, however, that, taking the nature of the /

the Mitscherlich method into account, a correlation coefficient of the order of 0.72 should be obtained. The Neubauer method is essentially a chemical method, although rye seedlings are used to extract the "available" potash instead of some chemical reagent, as in the case of the determination of the exchangeable potash. Mitscherlich's method is dependent on the applicability of his Growth Laws and on the value of the Effect Factor. It may be noted from equation 5 that the value of $x$ is inversely proportional to the value of 'C', the Effect Factor. If it is assumed that the total quantity of "available" potash is represented by the exchangeable content the fact that the Mitscherlich method gives, on the average, values representing 68% of the exchangeable potash may be due to the value of the effect factor used in the calculation being too high, or it may mean that, under the conditions of the pot experiments, the total quantity of exchangeable potash was not utilised by the plants. It is not possible to determine from the evidence at present available which explanation is correct, or even whether they are independent.

It has been mentioned previously that Mitscherlich has been forced to introduce a modification of his equation to account for the inconstancy in the values of 'c' obtained by several of his critics. A possible explanation of the observed discrepancies can be based on the supposition that a particular plant utilises a varying proportion of the total quantity of available nutrient under varying conditions of growth /

growth, and that the degree of utilisation varies with the species of plant under similar conditions of growth. It would still be possible under these assumptions that the increase in growth under standardised conditions should be a logarithmic function of the concentration of nutrient, but the proportionality constant or effect-factor would not be expressible in terms of total concentration but in terms of the fraction of this total quantity utilised or absorbed by the plant, this fraction varying with the plant species and with the external conditions of growth.

## III. S U M M A R Y of R E S U L T S.

(1) The potassium content in 34 soil samples from 13 soils typical of large areas in the East of Scotland has been determined by the methods of chemical analyses using

(A) hot concentrated hydrochloric acid, and

(B) 1% citric acid solution,

and the results compared with the concentration of potassium in the exchangeable state. The total mineral potassium has been determined for six samples and Neubauer's method of analysis has been applied to ten samples. Six samples of surface soil have been examined in detail to determine the correlation between the results given by the Mitscherlich and Neubauer methods.

(2) The average value of the total mineral potassium in the soils examined was 2.04% (as $K_2O$) which indicates the presence of comparatively large reserves of potassium in these soils. No relationship was found to exist between the total potassium and the quantities soluble in hot concentrated hydrochloric acid.

(3) The average value of the HCl-soluble potassium was 0.50% (as $K_2O$) and in the profile samples there was generally an increase in solubility with increase in depth of soil.

(4) /

(4) The citric soluble potassium had an average value of 0.0074% (as $K_2O$) which represents only 1.48% of that soluble in concentrated hydrochloric acid. In the profile samples the solubility generally decreased with increase in depth of soil with one marked exception in soil No.587.. The citric soluble potassium varied from 26 to 79% of the exchangeable potassium with a correlation coefficient of + .988 between the two series of values and it is suggested that the citric acid extraction is a case of partial base exchange.

(5) The figures obtained from the first series of Neubauer seedling analyses indicate a deficiency in available potassium in these samples. On comparison with the corresponding values of exchangeable potassium a correlation coefficient of + .989 is obtained between the two series. This would indicate that the concentration of exchangeable potassium determines the amount of $K_2O$ which can be absorbed by the seedlings.

(6) The second series of Neubauer analyses gave a similar correlation with the exchangeable potassium, but the correlation with the values deduced from the Mitscherlich experiments was not so significant, the coefficient being only + .735. This is not sufficient to conclude with certainty that the two methods are correlated, the probability against significance being about 0.1. The Mitscherlich /

Mitscherlich values represented on the average 68% of the exchangeable potassium, and since the concentrations deduced from the yield results are inversely proportioned to the magnitude of the "Effect-factor" it is concluded that (1) the Effect-factor is too high, or (2) the total quantity of exchangeable potassium is not available to the plants under the conditions of experiment. The latter assumption provides a possible explanation of some of the observations which have been advanced to disprove Mitscherlich's Growth Laws.

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